TREATMENT OF Fe(III) IONS FROM LEACHING SOLUTIONS WITH NEUTRALISATION AND PRECIPITATION

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ABSTRACT

The results of the study of leaching solutions (in the further text: productive solutions) from "BUCIM" mine treated with various neutralizing agents and combinations of two or a number of neutralizing agents are presented in this work.

Leaching of copper with sulfuric acid is forwarded with the leaching of many other elements which are present in the ores. Among the elements is Fe (III) which abuses the Cu^{2+} Ions in further processing in production of cathode copper. The main objective of the researches is the elimination of Fe(III) ions from the solutions by precipitation in $Fe(OH)_3$.

So, this creates the positive effects in the cathode copper production.

With suitably chosen neutralizer, following effects are achieved:

- *Raising the pH value to 4.0-4.5; and improving condition on the solutions for further processing;*
- *Removal of Fe (III) ions from the solutions to a concentrations of less than 0.1 g/L;*
- *Economic effects*

In doing so, found the optimum pH, which allows maximum precipitation of the iron^{3+} ions, and simultaneously the persistence of Cu^{2+}, in productive solutions.

KEYWORDS

Copper leaching, Neutralization, Cathode copper, $Fe(OH)_3$.

1. INTRODUCTION

The composition of the leaching solutions from BUCIM mine is a variable quantity in terms of several parameters, such as: the composition of the ore, concentration of sulfuric acid, temperature, pH value, etc. The invention relates to a method for the removal of iron (III) as $Fe(OH)_3$ sludge, from a copper(II)sulfate solution, in atmospheric conditions, during the electrolytic preparation of copper. Several copper ore types are included in the leaching processes with sulfuric acid, as the starting material in the electrolytic preparation of copper, such as: CuO, Cu_2O, CuS, $CuFeS_2$-where copper is also bound to iron in sulphidic form concentrations. The presence of FeS_2 is also inevitable. The amount of it is usually so considerable that recovering the Cu from it is unavoidable. CuO is easily soluble even at pH=2-

2.5 values, whereas Fe has to be leached at a higher acid content to encourages the leaching of the sulfide copper ores, as further process. This separate stage both copper and Fe are dissolved. Therefore the iron has to be precipitated from the solution obtained before the solution can be included in copper(II)sulfate concentration and purification and in the end for electrolysis. In industrial processes copper(II) sulfide leaching, an acid leach, is generally carried out at a pH 1.5-2 and iron leaching at an acid content between 30-100 g H_2SO_4/L. The solution formed, which contains the dissolved copper and iron, is very acidic, and can be neutralized before the iron is precipitated from it. Copper leaching can also be combined with the iron precipitation stage.

Nowadays, the leaching of copper ore is also combined with leaching of slug in even greater amounts. Depending on the process conditions, and the concentration of pyrite, and a chalcopyrite, as a side mineral, the amount of trivalent ferric iron in leaching solutions varies from 0.1 to 0.35 g/L, and the concentration of copper (II) ions from 0.3 to 1 g/L. Also, there are many other metal ions present in the solutions (traces) such as: Se, Te, Si, Ni, Zn, Co, Ag, Bi, Mn, Cr, Sb, Cd, As, P, Pb, Sn, etc.

2. METHODS

Acid neutralization on an industrial scale is usually accomplished by the treatment of acidic solutions by the manual or automatically controlled addition of a basic (alkaline) compound. Depending upon the characteristics of the individual base, bases are added as solids, solutions, slurries, or in the case of anhydrous ammonia, as a liquid or a vapor. Table 1 provides a comparison between equivalent weights of various bases:

Table 1: Pounds of chemical equivalent to one pound of the following acids

Chemical	Chemical formula	CH_3COOH	CrO_3	$C_6H_8O_7*H_2O$	HCl	HNO_3	H_3PO_4	H_2SO_4
Anhydrous ammonia	NH_3	0.28	0.34	0.24	0.47	0.27	0.52	0.35
Aqua ammonia 29.4%	NH_4OH	0.95	1.16	0.82	1.60	0.92	1.77	1.19
Calcium carbonate	$CaCO_3$	0.84	1.00	0.72	1.38	0.80	1.53	1.02
Caustic soda	NaOH	0.67	0.80	0.57	1.10	0.64	1.22	0.82
Slaked (Hydrated) Lime	$Ca(OH)_2$	0.62	0.74	0.53	1.02	0.59	1.13	0.76
Soda Ash	Na_2CO_3	0.88	1.06	0.76	1.45	0.84	1.62	1.08

Three iron precipitation processes are in use and in them the iron is precipitated as $Fe(OH)_3$. As the most compatible reagent for iron precipitation is ammonia. It is proved in laboratory conditions using precise volume of productive solution, 3% ammonia solution, pH meter-instrument, AAS – for quantitative analysis of metal ions present before and after the neutralizing process. The equation of the reaction between Fe and ammonia is:

$$Fe^{3+}(aq) + 3NH_3(aq) + 3H_2O(l) <==> Fe(OH)_3(s) + 3NH_4^+(aq) \quad (1)$$

The reaction of anhydrous ammonia neutralisation of sulfuric acid is shown below:

$$2NH_3+H_2SO_4\leftrightarrow(NH_4)_2SO_4 \quad (2)$$

Ammonia, by now, is used to increase pH in segments of the following industries

- Pharmaceutical
- Ore flotation
- Food
- And in this work it is proposed as most suitable reagent for the treatment of leaching solutions and to precipitate Fe(III) in $Fe(OH)_3$.

2.2 Equipment for acid neutralization with ammonia

Equipment requirements for acid neutralization for industrial uses with ammonia can vary from a very simple manual system to a more complex, fully automatic electronic system. If neutralization is done on a batch basis, a manual system with a portable pH meter should be adequate if proper records are kept. The design of a neutralization system should be approved by all concerned regulatory agencies.

The following type of control systems can be used for acid neutralization:

- Pneumatic System-control valve actuated by air pressure; control range plus or minus one pH unit;
- On-Off System-control valve actuated by electricity;
- Time Proportioning System-control valve actuated by electric timer;
- Position Proportioning System-position of control valve seat actuated by electricity.

2.1.1 System advantages of using ammonia for neutralization and precipitation

- Ammonia systems are simple. Since ammonia is stored under pressure, no transfer equipment is necessary and no external agitation is required in the neutralization pit
- Ammonia systems are reliable. With its own "built in" pressure system, no outside power source is required to operate transfer pumps, etc. high reliability is the result of system simplicity and minimum manpower requirement for the system operation.
- Ammonia systems are inexpensive; minimum equipment requirement, minimum handling and labor requirement, minimum maintenance due to reduced corrosion of piping, controls etc.
- Minimum space requirement for total system.
- Ammonia systems are flexible. Equipment layouts can be simple and inexpencive for manual operation, or completely automatic electronic systems can be installed.

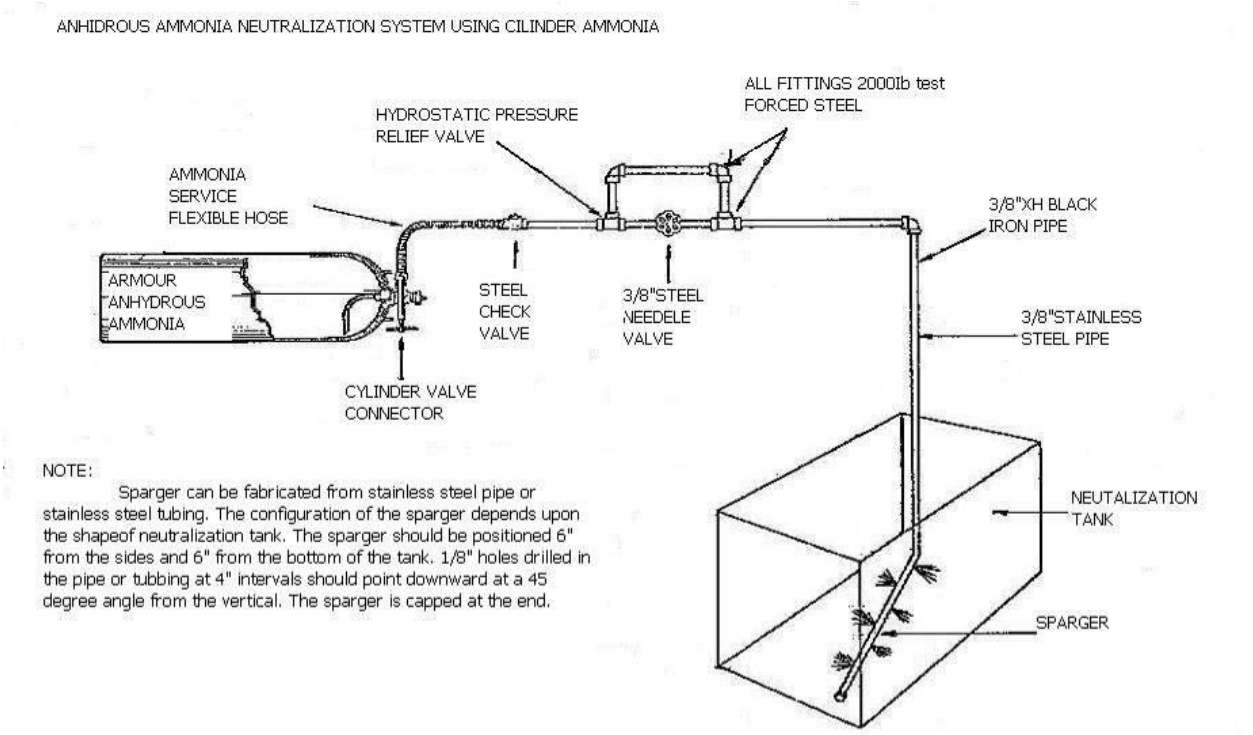

Figure 1: Ammonia neutralization system

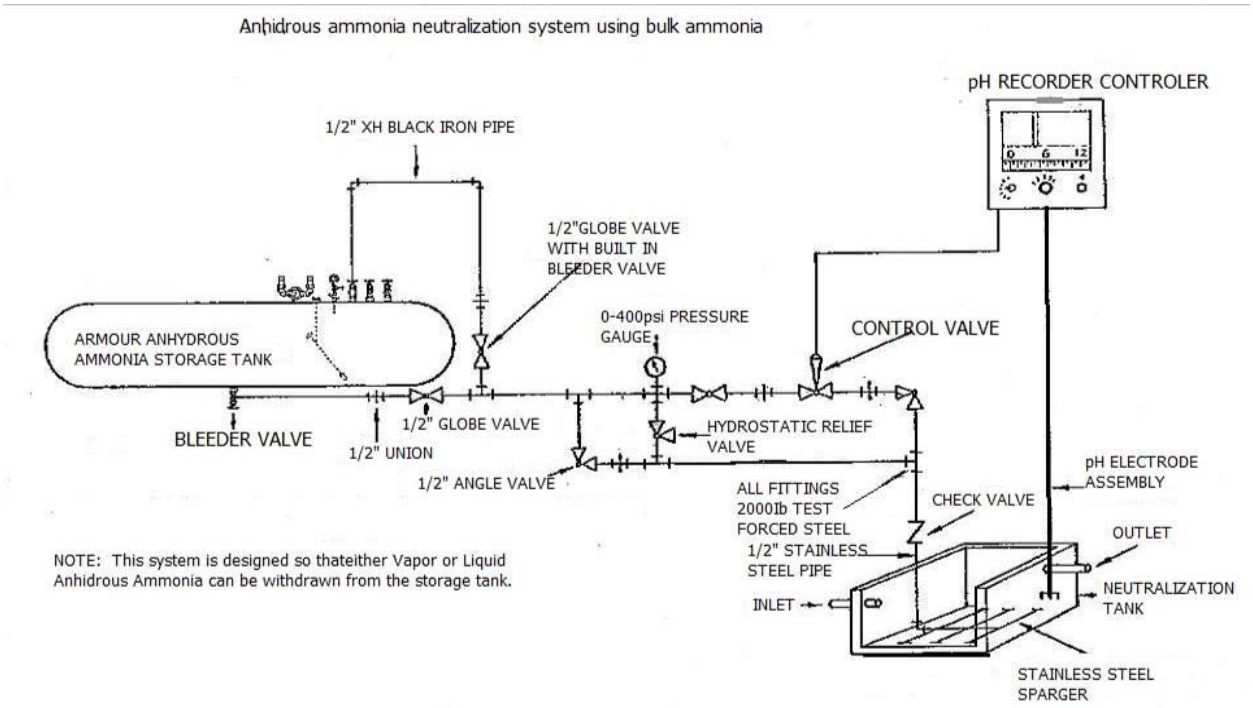

Figure 2: Neutralization system using bulk ammonia

Figure 1 shows a basics system layout for an acid neutralization system using anhydrous ammonia cylinders. Figure 2 shows a basic acid neutralization system using bulk anhydrous ammonia. Each system should be designed to fit the requirements of a specific situation. The Sparger design is dependent upon the size and shape of the neutralization pit. It is generally desirable to locate the pH electrode near the neutralization pit outlet.

2.2 Other alternative neutralizers

Under controlled conditions, productive solutions can be neutralized using $CaCO_3$, as opposed of lime. Limestone can remove acidity and precipitate iron. Limestone dissociates and CO_2 gas evolves, as shown below:

$$CaCO_{3(s)} + H_2SO_{4(aq)} \leftrightarrow CaSO_{4(s)} + H_2O + CO_{2(g)} \quad (3)$$

$$CaCO_{3(s)} + Fe_2(SO_4)_{3(aq)} + 3H_2O \leftrightarrow 3CaSO_{4(s)} + 2Fe(OH)_{3(s)} + 3CO_{2(g)} \quad (4)$$

Released CO_2 gas forms carbonate ion which acts as a buffer and sets an upper limit on pH (max pH=6.5) and also affects the rate and amount of lime consumption. The precipitates may settle very slowly because of their small particle site. Removal of a board range of metals can be achieved at higher pH levels than 6.5. Therefore, pH must be continuously monitored and kept in ranges optimized for precipitate only Fe^{3+} ions.

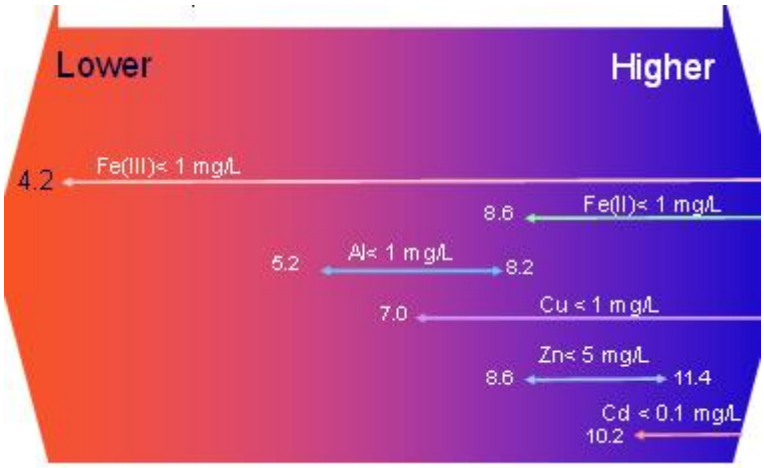

Figure 3: Range of pH suitable for metal hydroxide precipitation

Sodium hydroxide (NaOH); this is expensive reagent and the resulting sludge does not settle well, requiring filtering in most cases. But it has high reactivity and results in less voluminous sludge.

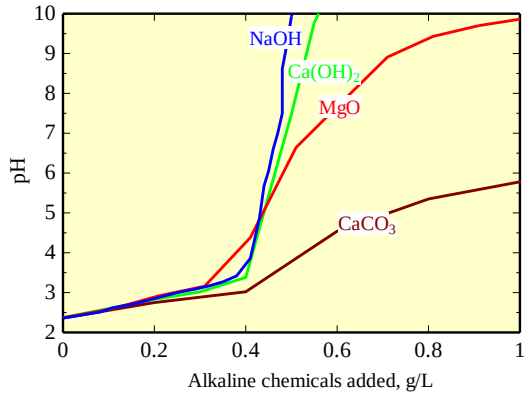

Figure 4: Titration curves for synthetic AMD with various alkaline reagent

3. RESULTS AND DISCUSSION

For the experiments 100 ml volume of productive solution is used and measured on pH meter and its pH_1 =2.43. Copper (II) and total ferrous and ferry ions are analysed on AAS before and after treatment with NH_4OH, 3% solution. Neutralization process with ammonia is limited to optimum pH range of 4.5. As a result, a yellow sludge of $Fe(OH)_3$ is present in the solution. Then the solution is filtrated and the sludge is drought and its mass is measured. By the end

another amount of productive solution is treated with ammonia, and then with 180g/L H_2SO_4. The obtained sludge of $Fe(OH)_3$ re-dissolves. Therefore here we have so called homogeneous precipitation where the precipitate ions on determined pH, return back to solution with decreasing of pH with sulfuric acid. The results from experiments are given in table 2:

Table 2: dependence of concentration of Cu and Fe with neutralization with 3% NH_4OH and increasing of pH

pH_1	$\gamma_1(Fe)$/[mg/L]	$\gamma_1(Cu^{2+})$/[mg/L]	$V(NH_4OH)$/mL	pH_2	$\gamma_2(Fe)$/[mg/L]	$\gamma_2(Cu^{2+})$/[mg/L]
2.53	295	532	1	3.10	290	532
3.10	290	532	1	3.45	290	532
3.45	290	532	1	4.01	153	532
4.01	113	532	1.5	4.43	8	521
4.43	8	521	0.1	4.52	1	520

pH_1- pH value before treatment with neutralizer

pH_2- pH value after treatment with neutralizer

The ammonia solution is added slowly in small amounts. During that time the solution is mixed with glass rod and in the solution the electrode from pH meter is immersed. This reaction of neutralization is fast and lasts a several minutes. Also, creating sediment is quickly and easy.

From the results, on pH value 4.52 concentration of Fe reduces from 290 to 1 mg/L, and on the other hand the mass concentration of Cu^{2+} is practically not changed. Opposite process, decreasing of pH, by lowering the pH to values less than 3 pH units, with sulfuric acid, gives the ions of Fe back in the solution.

Table 3: Efficiency of Fe removal from leaching solutions

pH value	The efficiency of Fe_{total} removal/%
4.01	47.24
4.43	97.24
4.52	99.65

The sludge is filtrated and dried in a dryer on 105°C for a half an hour. Then the mass of the sludge is measured on analytical Libra together with filter paper. Before that the filter paper is measured empty. The mass of the pure sludge is 1.365g.

If 100 mL productive solution are receiving 1.365g sludge, from 11000m^3 solutions 150t sludge. Therefore the sludge must be simultaneously treated. The application requires large tanks and separators. However, the main achievement is that the production of cathode copper will increase for 20-25%, so that the investment is worthwhile.

4. CONCLUSION

With the application of this experimental laboratory experiments in industrial processes of leaching solutions in "BUCIM" mine can be very useless with the application of simple neutralizing systems given above. The following benefits can be obtained:

- Removing iron from the leaching solutions
- Increasing of pH (more suitable for adsorption of copper in the first phase of concentration of copper ions)
- Increasing concentration of copper in regenerate (product of the first phase of processing electrolysis of copper) that much as it is the concentration of Fe in primary solutions, because in the first step ion changer adsorbs trivalent ferry ion with the same selectivity as adsorption of copper 2+ ions.
- Increase the percentage of utilization of copper ions, and achieving better economic effects in all production of cathode copper

Removing of sludge of $Fe(OH)_3$ can be performed in two ways:

- With well known vacuum filter or centrifuge, because of very high fluidity of sludge, or
- With their re-dissolving in solution and return back on irrigation fields, where they can support the leaching of the sulfide copper ores.

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